

AD-A278 459



2

OFFICE OF NAVAL RESEARCH

Grant N00014-93-1-0351

R & T Code 4133020- -09

Technical Report No.7

The Kinetics of Heterogeneous Electron Transfer Reactions in Polar Solvents

by

W. Ronald Fawcett and Marcin Opallo

Prepared for Publication

in

Angewandte Chemie International Edition in English

Department of Chemistry
University of California
Davis, CA 95616

April 20, 1994

Reproduction in whole or in part is permitted
for any purpose of the United States Government

"This document has been approved for public release
and sale; its distribution is unlimited"

94-12409



580

DTIC QUALITY INSPECTED 3

94 4 22 105

DTIC
ELECTE
APR 25 1994
S B D

REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 20, 1994		3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE The Kinetics of Heterogeneous Electron Transfer Reactions in Polar Solvents.				5. FUNDING NUMBERS N00014-93-1-0351	
6. AUTHOR(S) W.R. Fawcett and M. Opallo					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of California Davis, CA 95616				8. PERFORMING ORGANIZATION REPORT NUMBER No. 7	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Arlington, VA 22217-5000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared for publication in Angewandte Chemie International Edition in English.					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unclassified				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Data for heterogeneous electron transfer reactions obtained in the last ten years have been examined within the context of contemporary theory. Special attention is focussed on systems for which rate constants and activation parameters are available as a function of the solvent, and as a function of temperature. The role of reactant structure in determining the kinetic parameters is also considered. Double layer effects both at unmodified and modified electrodes are discussed in detail. Experimental techniques, especially those suited to measuring fast reactions, are also outlined.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	
				20. LIMITATION OF ABSTRACT unclassified	

A Review

The Kinetics of Heterogeneous Electron Transfer Reactions in Polar Solvents

by William Ronald Fawcett* and Marcin Opallo

Data for heterogeneous electron transfer reactions obtained in the last ten years have been examined within the context of contemporary theory. Special attention is focused on systems for which rate constants and activation parameters are available as a function of the solvent, and as a function of temperature. The role of reactant structure in determining the kinetic parameters is also considered. Double layer effects both at unmodified and modified electrodes are discussed in detail. Experimental techniques, especially those suited to measuring fast reactions, are also outlined.

*Professor W.R. Fawcett
Department of Chemistry
University of California
Davis, CA 95616

Dr. M. Opallo
Institute of Physical Chemistry
Polish Academy of Sciences
01-224 Warsaw, Poland

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

1. Introduction

Since the early 1980's there has been a great increase in interest in medium effects for electron transfer (ET) reactions. This revival was spurred by the appearance of several theoretical papers [1-4] which predicted the existence of solvent dynamical effects in the kinetics of ET. The first experimental evidence for a dynamical effect in a heterogeneous ET reaction was presented by Kapturkiewicz and Behr [5]. This was quickly followed by a report describing similar effects for a homogeneous ET reaction [6]. Since then a significant body of experimental evidence has been described in the literature relating to solvent and other medium effects. These experiments have focused on three areas namely, homogeneous self-exchange ET, heterogeneous ET, and time-resolved fluorescence spectroscopy involving intramolecular ET. At the same time, significant advances have been made in the theoretical description of ET processes.

Several recent reviews have focussed on the development of theory of this elementary reaction and its application to experimental results [7-9]. Heitele [9] has examined in a particularly lucid and useful manner the theory of dynamic solvent effects in ET. On the experimental side, Barbara and Jarzeka [10] have reviewed experimental results in time resolved fluorescence spectroscopy. Weaver [11] has discussed data for homogeneous ET reactions, especially those obtained in his laboratory.

The subject of the present review is heterogeneous ET. The discussion is limited to simple reactions, that is, those in which both oxidized and reduced forms remain in solution, only one electron is transferred, and no chemical bonds are broken or formed. Since the original work of Kapturkiewicz and Behr [5] on dynamic solvent effects, a large number of related studies have appeared in the literature. Our goal is to examine these results within the context of contemporary theoretical development and show their relationship to other experiments describing medium effects in ET. No attempt is made here to discuss theory in detail since this has already been done [7-9]. However, a few aspects of theory which were

not considered in previous reviews and which are particularly relevant to the analysis of experimental data are considered. As well as presenting the important results obtained, advances in experimental techniques are also discussed. It is important to emphasize that the improved understanding of the role of the medium in ET has been due in great part to the fact that faster processes in condensed media can now be followed experimentally with precision. Finally, it should be pointed out that heterogeneous ET is usually studied in the presence of an inert electrolyte in order to improve solution conductivity and maintain diffusion as a means of mass transfer. As a result, the medium for the ET reaction involves not only the solvent but the ions of the electrolyte which form the double layer at the electrode. Double layer effects play an important role in heterogeneous ET and are also considered in this review.

2. Theory

2.1 Estimation of the Activation Parameters

One of the important problems considered in recent years is improvement of the estimation of the Gibbs energy of activation ΔG^* and related kinetic parameters. ΔG^* is traditionally regarded as composed of two parts, the inner sphere contribution ΔG_{is}^* and the outer sphere contribution ΔG_{os}^* [12]. Estimation of the former requires a description of the changes in bond lengths and angles which accompany the activation process, and is often based on the appropriate spectroscopic data [13]. The outer sphere component which accounts for the work done to reorganize the solvent atmosphere around the reactant has usually been estimated on the basis of a model based on the Born theory of ionic solvation [12, 13]. In the case of the simple heterogeneous ET reaction,



this contribution is given by

$$\Delta G_{os}^* = \frac{N_0 e_0^2}{32\pi\epsilon_0} \left(\frac{1}{r_A} - \frac{1}{R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (2)$$

where N_0 is the Avogadro constant, e_0 , the fundamental electronic charge, r_A , the radius of the reactant A represented as a sphere, R , the distance from its image in the electrode, ϵ_{op} , the optical relative permittivity of the solvent, ϵ_s , the static value, and ϵ_0 , the permittivity of free space. An important point in application of this relationship is estimation of r_A since most reactants are not spherical. This aspect is considered in more detail below. In estimating ΔG_{os}^* in recent work, it has usually been assumed that the distance, R , is effectively infinity, the stabilizing effect of any image formed in the electrode being neglected. Certainly, in cases where the ET reaction remains simple in the sense that the reactant and product do not interact with the electrode itself, R is equal to $2r_A + 2d_i$ where d_i is the thickness of the layer composed of solvent and closest approaching counter ions between the reactant and the geometrical electrode/solution interface. Thus, R corresponds at least to three molecular diameters, that is, it is the order of six times r_A . Moreover, the efficiency with which the image is formed in the electrode can be questioned on the basis of the spatial dispersion of the solvent dielectric permittivity and electric field penetration into the metal electrode [14, 15]. Kornyshev et al. [14, 15] applied the non-local electrostatic treatment to estimation of ΔG_{os}^* for both heterogeneous and homogeneous ET reactions, and concluded that this quantity actually increases as the reaction site moves closer to the electrode instead of decreasing as predicted by equation (2). However, the sharp boundary model used in these calculations [15] can be criticized because it is not applicable in regions where the dielectric properties of the system are changing markedly over short distances, that is, near a reactant at the reaction site in the double layer. Nevertheless, on the basis of a comparison of activation enthalpies for the same reaction under homogeneous and heterogeneous conditions (*vide infra*) it seems clear that R is sufficiently large that $1/R$ can be neglected in estimating ΔG_{os}^* for the heterogeneous process. This assumption is made in the following discussion.

Further improvements in the estimation of ΔG_{os}^* have involved the use of non-primitive models for ionic solvation, especially the mean spherical approximation (MSA) [16, 17]. On the basis of the hypothetical two step charging process associated with thermal electron transfer described by Marcus [18], ΔG_{os}^* can be regarded as giving the difference between the Gibbs solvation energies of the reacting system at optical frequencies and at static frequency. This can be seen when equation (2) is rewritten as

$$\Delta G_{os}^* = - \frac{N_0 \epsilon_0^2}{32 \pi \epsilon_0 r_A} \left(1 - \frac{1}{\epsilon_{op}} \right) + \frac{N_0 \epsilon_0^2}{32 \pi \epsilon_0 r_A} \left(1 - \frac{1}{\epsilon_s} \right) \quad (3)$$

in a form which clearly shows the relationship of the Marcus model to the Born continuum model for ionic solvation. Following earlier work of Wolynes [19], McManis and Weaver [20] wrote expression (4) for ΔG_{os}^* in the MSA:

$$\Delta G_{os}^* = - \frac{N_0 \epsilon_0^2}{32 \pi \epsilon_0} \left[\left(1 - \frac{1}{\epsilon_{op}} \right) \frac{1}{(r_A + r_s / \lambda_{op})} - \left(1 - \frac{1}{\epsilon_s} \right) \frac{1}{(r_A + r_s / \lambda_s)} \right] \quad (4)$$

where r_s is the radius of a solvent molecule represented as a sphere, and λ_{op} and λ_s , polarization parameters estimated from ϵ_{op} and ϵ_s , respectively by equations (5) and (6).

$$16 \epsilon_{op} = \lambda_{op}^2 (1 + \lambda_{op})^4 \quad (5)$$

and

$$16 \epsilon_s = \lambda_s^2 (1 + \lambda_s)^4 \quad (6)$$

In its application to ion solvation at static frequencies [21], the parameter, λ_s , accounts for the polarizability, softness, and non-sphericity of the solvent molecule which is otherwise represented as a hard sphere with a central point dipole. For polar solvents, the value of λ_s is in the range 2.0 to 2.9 [22], so that the MSA estimate of the static contribution to ΔG_{os}^* is considerably reduced from the Born estimate. In the case of the high frequency solvation, λ_{op} is a number close to unity, so that the estimate of the optical contribution to

ΔG_{os}^* is also greatly reduced in magnitude from the continuum value. However, there is a serious question whether the MSA model developed for a system of hard spheres with point charges and point dipoles at static frequencies [19-22] can be applied at optical frequencies where there is no orientational contribution to dipolar polarization [23]. Thus, the McManis-Weaver (MW) model [20] can be questioned within the context of the MSA.

A quite different approach to applying the MSA to estimation of ΔG_{os}^* was taken by Fawcett and Blum (FB) [23]. Firstly, they assumed that the optical contribution is given to a good approximation by the Born estimate. Secondly, the polarization parameter at static frequencies was obtained from estimates of the Gibbs solvation energies of simple monoatomic monovalent ions rather than from equation (6). As a result, the expression for ΔG_{os}^* becomes

$$\Delta G_{os}^* = - \frac{N_0 e^2}{32 \pi \epsilon_0} \left[\left(1 - \frac{1}{\epsilon_{op}} \right) \frac{1}{r_A} - \left(1 - \frac{1}{\epsilon_s} \right) \frac{1}{(r_A + r_g \lambda_i)} \right] \quad (7)$$

where the parameter λ_i depends on whether the ion is a cation or an anion but not on its size. Stated otherwise, the FB model predicts that the Gibbs activation energy to form a monovalent cation from a neutral molecule via electrooxidation is different from that to form a monovalent anion from the same reactant via electroreduction, all other system parameters remaining the same. This follows from the experimental observation that the extent of solvation of cations and anions of the same radius in a given solvent is not the same [24].

Two other activation parameters, namely, the enthalpy ΔH_{os}^* and entropy of activation ΔS_{os}^* may be estimated given the temperature coefficient of the Gibbs energy. From equation (3) estimation of ΔS_{os}^* on the basis of the Born model requires knowledge of the temperature coefficients $d\epsilon_s/dT$ and $d\epsilon_{op}/dT$ which are available for all polar solvents used in electrochemical studies [24, 25]. In the case of the MW model, one also needs the temperature coefficients $d\lambda_{op}/dT$ and $d\lambda_s/dT$ which may be obtained from the experimental

coefficients $d\epsilon_s/dT$ and $d\epsilon_{op}/dT$ after differentiating equations (5) and (6) with respect to temperature [22]. Finally, one needs the temperature coefficient $d\lambda_i/dT$ in the FB model. These quantities were extracted from experimental solvation entropy data for the alkali metal cations and halide anions [22]. Once one has estimated ΔS_{OS}^* , the activation enthalpy ΔH_{OS}^* can be found by adding $T\Delta S_{OS}^*$ to the estimate of ΔG_{OS}^* .

Values of ΔG_{OS}^* and ΔH_{OS}^* estimated by the various models described here in twelve polar solvents are summarized in Table 1. The reactant size parameter λ_A was set equal to 0.37 nm, a value appropriate for the metallocenes [26] whose ET kinetics have been studied extensively both homogeneously and heterogeneously [11]. The first observation one may make is that the estimates of ΔG_{OS}^* and ΔH_{OS}^* differ by only a few kJ mol^{-1} at the most, the difference being negligible on the basis of the MSA for most solvents. However, estimates based on the MSA differ considerably depending on the assumption made regarding the high frequency contribution, and the method of estimating the polarization parameter at low frequencies. Estimates of ΔG_{OS}^* on the basis of the MW model are about 90 percent of those obtained by the continuum Marcus model. On the other hand, using the FB model, the estimates of ΔG_{OS}^* fall to 62 percent of the Marcus estimate for a reaction involving cations, and 80 percent for a reaction involving anions. These differences are significant and should be seen experimentally.

The major problem with the MSA approach is that a proper estimate of ion-dipole interactions at high frequencies has yet to be made. Some support for the FB assumption is found from the finding that the MSA estimates of the dielectric properties of a polar solvent at optical frequencies agree well with those based on classical models [27]. However, the separate problem of ion-dipole interactions at high frequencies needs to be addressed as well.

2.2 Estimation of the Pre-Exponential Factor

Much has been written already about the pre-exponential factor in the rate constant for ET especially with respect to dynamic solvent effects [1-4, 7, 9, 11]. The discussion here is limited to those aspects which relate to heterogeneous ET and to appropriate expressions for the rate constant. On the basis of transition state theory formalism [13], the standard heterogeneous rate constant is usually written as

$$k_s = \kappa K_p \nu_n \exp(-\Delta G^*/RT) \quad (8)$$

where κ is the electronic transmission coefficient, K_p , the encounter pre-equilibrium constant, and ν_n , the nuclear barrier-crossing frequency. κ is unity for an adiabatic reaction and falls below unity as the extent of diabaticity increases. The extent of diabaticity is connected with the degree of interaction between the free energy surfaces for the reactant and product and is determined by the electronic matrix coupling element H_{ab} [13]. The value of H_{ab} can also affect the nuclear barrier crossing frequency, ν_n , so that when H_{ab} is large and the barrier rounded, ν_n falls below the value which it has for small values of H_{ab} [4, 28]. Simple relationships connecting these quantities are given by the Landau-Zener model [13] according to which the electron tunnelling frequency is given by equation (9),

$$\nu_{el} = \frac{2H_{ab}^2}{N_0 h} \left(\frac{4\pi^3}{\Delta G^* RT} \right)^{1/2} \quad (9)$$

where N_0 is Avogadro's constant and h , Planck's constant. The electronic transmission coefficient is then given by equation (10).

$$\kappa = \frac{2[1 - \exp(-\nu_{el}/2\nu_n)]}{2 - \exp(-\nu_{el}/2\nu_n)} \quad (10)$$

When $\nu_{el} \gg \nu_n$, κ is unity and the reaction is adiabatic. However, when $\nu_{el} \ll \nu_n$, the expression for κ becomes

$$\kappa = \nu_{el} / \nu_n \quad (11)$$

and electron tunnelling controls the magnitude of the pre-exponential factor. This diabatic limit occurs in cases where the extent of interaction between the reactant and electrode is minimized, for instance, in the presence of a blocking film on the electrode. In this case H_{ab} is small, ν_{e1} falls, and κ is given by equation (11). Obviously, the structure of the electrode/solution interface plays an important role in determining these quantities.

The encounter pre-equilibrium constant K_p has been defined within the context of the encounter pre-equilibrium model for heterogeneous ET reactions [29] and contains any double layer terms and steric effects. In the absence of the latter effects, it has been estimated to be approximately 60 pm for a spherical reactant [29]. Thus, after correction for double layer effects, the upper limit for the product κK_p is ~60 pm. Lower values can be due to steric effects or departure from reaction adiabaticity. Because of the very approximate nature of the models used to estimate κ and K_p individually, it is preferable to cite only the product κK_p on the basis of an analysis of experimental data [30].

The nuclear barrier-crossing frequency ν_n depends on vibrational modes within the reactant and solvent modes to an extent which is contingent upon the relative importance of the inner and outer sphere contributions to the activation barrier. When the reaction is adiabatic and the inner sphere contribution to ΔG^* is small, this frequency is given by equation (12) [1-4]

$$\nu_n = \tau_L^{-1} \left(\frac{\Delta G^*}{4\pi RT} \right)^{1/2} \quad (12)$$

where τ_L is the longitudinal solvent relaxation time. For Debye solvents in the continuum approximation, τ_L is given by [31]

$$\tau_L = \frac{\epsilon_\infty \tau_D}{\epsilon_s} \quad (13)$$

where ϵ_∞ is the high frequency relative solvent permittivity and τ_D , the Debye relaxation time. Values of τ_L have been collected for a large number of polar solvents [32] whose behaviour

follows the Debye model to a good approximation. Thus, the pre-exponential factor is predicted to depend on the solvent's dielectric relaxation properties, parameters which are quite different in origin to those which determine the Gibbs activation energy barrier.

When the inner sphere activation barrier is large, and/or when the reaction adiabaticity is weak, the dependence of the pre-exponential factor on solvent is weakened. A convenient approximate way of writing the nuclear barrier crossing frequency, ν_n , is then equation (14) [33]

$$\nu_n = \nu_{is}^{1-\theta} \tau_L^{-\theta} \quad (14)$$

where ν_{is} is the frequency associated with an intra-molecular vibration. Combining equations (8) and (14), one may express the standard rate constant using equation (15)

$$k_s = A \tau_L^{-\theta} \exp(-\Delta G^\ddagger/RT) \quad (15)$$

where the factor A contains all the contributions to the pre-exponential factor which to a first approximation do not depend on the solvent and θ is a fraction between 0 and 1. This way of expressing the solvent dependence was first given by McGuire and McLendon [34] and is especially convenient for discussing the experimentally observed solvent dependence. It is also suggested by the theoretical analysis presented by Nadler and Marcus [35]. An unattractive feature of equation (15) is that the factor A has fractional dimensions of time when θ is a fraction [33].

The nuclear barrier crossing frequency on the basis of known values of ν_{is} and τ_L is the order of 10^{12} to 10^{14} s^{-1} . As a result, the upper limit for the pre-exponential factor for heterogeneous ET is approximately 6000 cm s^{-1} . For a reaction with a Gibbs energy barrier of 20 kJ mol^{-1} , this corresponds to a standard rate constant of 2 cm s^{-1} at 25°C . This estimate is certainly of the correct order of magnitude in terms of kinetic data collected to date.

Some mention should be made of solvents which do not follow the simple Debye model. Most solvents exhibit multiple relaxation when the frequency dependence of the dielectric permittivity is examined over a sufficiently wide range [36]. Estimation of τ_L is more complex for these systems [37], but can be made on the basis of the work of Hynes [28]. Solvents for which non-Debye behaviour is important are the alcohols, and protic amides [36]. In these systems τ_L is a function of time [37], the value observed at very short times (high frequency limit) being relevant to the type of reaction being considered here. Thus, when τ_L for the alcohols was estimated considering the relaxation modes at higher frequencies, the kinetic data obtained in these solvents falls into line with those obtained in simpler solvents [33].

As a note of caution, it should be remembered that the Debye model on which the estimation of τ_L is based is a continuum model, and therefore does not recognize the unique properties of the solvent in the vicinity of the reactant. Thus, the local value of τ_L may be quite different from that estimated on the basis of the Debye parameters (equation 13). However, the fact that one obtains clear correlations between $\ln k_s$ and $\ln \tau_L$ for the majority of systems studied to date suggests that there is a simple relation between the actual local relaxation time and that estimated by the Debye model. This problem can be elucidated using ultra fast spectroscopic relaxation techniques and work in that direction has been initiated [10].

Finally, it should be noted that the above discussion has been made within the context of Marcus theory which strictly speaking was developed for adiabatic reactions [12]. Electronic effects are included in this model heuristically by way of the electronic transmission coefficient κ . An alternative approach is that of Dogonadze [38] which is based on a quantum mechanical description of a manifold of potential energy surfaces. The quantum mechanical approach was recently extended by Schmickler [39] and its relationship to relevant experimental observations discussed in detail.

3. New Developments In Experimental Methods

In order to test the predictions made by contemporary theory, one must be able to determine the standard rate constants for fast heterogeneous ET reactions. Efforts in this direction have most often involved ultramicroelectrodes [40-42]. When these are used as working electrode, the current flowing in the electrochemical cell is typically 100 to 1000 times smaller than that at a conventional dropping mercury electrode so that problems due to iR drop and capacitive current are greatly reduced. Ultramicroelectrodes are often metal wires with diameters of the order of microns which are sealed in glass so that a disc is exposed to the electrolyte solution. Electrode materials include platinum, gold and carbon, and must be carefully polished before each experiment. The gold disc electrode may be modified to a mercury hemisphere by electrodeposition of mercury [43,44], or by exposing the gold disc to a pool of highly purified mercury for a short time [45]. Attempts have also been made to fabricate electrodes of nanometer dimensions, so called "nanodes" [46]. However, the area of the conducting material exposed to the solution is extremely difficult to define due to problems in sealing glass to metal rods of such small diameter [47]. As a result interpretation of current-voltage data with a view to obtaining kinetic information is impossible [47,48].

The most popular technique for determining kinetic parameters using ultramicroelectrodes has been cyclic voltammetry using fast scan rates [42, 49, 50]. However, extraction of the kinetic information is not straightforward and requires careful analysis of the effects of any uncompensated iR drop [51].

Another technique introduced recently by Baranski [43, 44, 52-54] is high frequency a.c. admittance voltammetry at ultramicroelectrodes. By working at higher frequencies linear mass transfer conditions are maintained at the working electrode. Moreover, the resistance of the system, and interfacial capacitance are monitored directly in the experiment so that any problems with the state of the electrode/solution interface are easily recognized. Baranski

[54] has carried out a detailed analysis of the possible errors in these experiments and shown how one may optimize the frequency range for a kinetic study given the electrode area, solution resistance, and double layer capacity. These experiments involve a fairly simple extension of well known admittance methods [55, 56] and are easily performed at frequencies up to 100 kHz. As a result, there is no problem in determining rate constants up to 10 cm s^{-1} with reasonable precision [44, 45, 53, 57].

Bard and coworkers [58-61] have demonstrated that scanning electrochemical microscopy may be used to determine fast ET kinetics precisely. In such an experiment, a micron-sized ultramicroelectrode, which is normally used to probe the surface of a substrate and is very close to it, acts as a working electrode with the reactant dissolved in the small volume of solution between the ultramicroelectrode and the closely positioned substrate. They have shown that mass transfer conditions are such that one can measure fast ET kinetics in both aqueous [58, 59] and highly resistive non-aqueous media [60, 61]. Results from these experiments for the electrooxidation of ferrocene in acetonitrile [59] and the electroreduction of buckminsterfullerene in benzonitrile [61] agree well with data obtained earlier using high frequency a.c. admittance methods [53, 57].

Osteryoung et al. [62, 63] have described a short time pulse voltammetric technique for studying fast heterogeneous reactions at ultramicroelectrodes. In the normal pulse mode, the electrode potential is stepped to a potential where a faradaic process occurs and held at the final potential for a fixed time which is the order of microseconds, and the resulting current transient recorded [62]. The kinetic information is obtained from the faradaic current measured towards the end of the pulse. The electrode is held at the initial potential for a time which is the order of milliseconds so that the effects of mass transfer near the electrode are obliterated by diffusion before the next pulse to a new final potential is applied. This technique was recently applied to determining standard rate constants for ferrocene and anthracene in acetonitrile and dichloromethane [63].

Mahlendorf and Heinze [64] have recently used impedance spectroscopy to study fast electron transfer reactions at a Pt electrode of conventional size in highly resistive non-aqueous media. Their method of data analysis differs significantly from that used by Baranski [44, 54] and requires the extraction of five parameters using non-linear regression. They obtained a standard rate constant for the oxidation of ferrocene in dichloromethane which is slightly less than that found by a.c. admittance techniques at ultramicroelectrodes [53] when one considers the fact that their experiments were carried out at a higher temperature (293 K). These authors [64] were unsuccessful in obtaining kinetic data in acetonitrile.

Some feeling for the experimental problems involved in determining rate constants for fast heterogeneous reactions can be obtained by comparing data reported recently by various laboratories for the kinetics of electrooxidation of ferrocene in acetonitrile (see Table 2). Acetonitrile is a solvent of low viscosity with a short longitudinal relaxation time (~ 0.2 ps), and ferrocene is a reactant with a low inner sphere reorganization energy. These factors combine to make ET rapid in this system. Examination of the data summarized in Table 2 reveals an unacceptably large range for rate constants reported during the last seven years, namely, from $2 \times 10^{-2} \text{ cm s}^{-1}$ to 220 s^{-1} , that is by four orders of magnitude! If the two low results [66, 67] and the high result [46] are removed a much more acceptable range, from 1 to 4 cm s^{-1} , is found. It should be noted that differences in electrolyte nature and concentration, and in temperature cause some of the observed scatter in the remaining data. The very high result by Penner et al. [46] is almost certainly due to problems in defining the area of the electrode exposed to the solution when electrodes of diameters significantly less than $1 \mu\text{m}$ are used [47, 48, 60]. The same comment can be applied to the low result of Russell et al. [66] who used a ring microelectrode. The low result reported by Abbott et al. [67] at an electrode of conventional dimensions is attributed to uncompensated iR drop. The results obtained by fast scan cyclic voltammetry at ultramicroelectrodes [49, 50, 65] fall somewhat below the most recent result by Mirkin et al. [60], probably as a result of some

uncompensated iR drop [51] and effects due to non-linear diffusion [60, 68]. The rate constant estimated from the data of Baranski et al. [53] on the basis of available temperature coefficient data [53, 69, 70] is 3.8 cm s^{-1} at 298 K. Thus, the standard rate constant for this reaction determined by scanning electrochemical microscopy and high frequency a.c. admittance agree with one another within experimental error. The recent result of Karpinski and Osteryoung [63] falls somewhat below these for reasons which are difficult to assess but which also may be related to uncompensated iR drop.

The above results demonstrate that one must exercise great care in the measurement of fast ET kinetics. However, it is clear that experimental techniques are now available which can provide precise data for rapid reactions. This means that important theoretical questions can be examined on the basis of reliable experimental data.

4. Effects Of The Solvent

The major focus of experimental work during the last ten years has been to understand the role of the solvent [71, 72]. These studies have shown clearly that a dynamic solvent effect is present especially when the inner sphere reorganizational energy is small. The presence of a dynamic effect is most easily demonstrated by plotting the standard rate constant measured in various solvents against the solvent's longitudinal relaxation time on logarithmic scales. Data for the electrooxidation of ferrocene [53] and 1,4-diaminobenzene [73] are shown in Figure 1. Quite good linear relationships are obtained between these two quantities, the slope for the 1,4-diaminobenzene system being less than that for the ferrocene system. The scatter observed is attributed to the fact that the variation in ΔG_{os}^* with solvent is ignored in making such a plot. On the basis of equation (15), the exact relationship between $\ln k_s$ and $\ln \tau_L$ is

$$\ln k_s = \ln A - \theta \ln \tau_L - \Delta G_{is}^*/RT - \Delta G_{os}^*/RT \quad (16)$$

The results obtained for many systems [5, 45, 53, 69, 73-79] support the conclusion that variation in $\ln \tau_L$ is significantly greater than variation in $\Delta G_{OS}^*/RT$ for a typical selection of polar solvents. In early work [5], it was also pointed out that a correlation exists with the logarithm of the solvent's viscosity.

Considerable discussion has centered on the separation of the solvent effect due to the pre-exponential factor from that due to the Gibbs energy barrier [11, 31, 33, 40]. If both τ_L and ΔG_{OS}^* are known, the parameters Δ and θ , are easily determined using linear regression techniques. In most cases ΔG_{OS}^* is either unknown or difficult to estimate. However, on the basis of the Marcus model [12], it is proportional to the solvent's Pekar factor, $1/\epsilon_{op} - 1/\epsilon_s$. An approximate linear relationship between ΔG_{OS}^* and the Pekar factor is also found when the former quantity is estimated using the FB model [22]. Thus, equation (16) can be written in the approximate form

$$\ln k_s \equiv K - \theta \ln \tau_L - g \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (17)$$

where K is a solvent independent constant and g , the proportionality constant relating ΔG_{OS}^* to the Pekar factor. Thus, the parameters θ , g and K can be determined on the basis of a two parameter regression with $\ln \tau_L$ and the Pekar factor as independent variables [30]. Such an analysis requires that $\ln \tau_L$ and $(1/\epsilon_{op} - 1/\epsilon_s)$ not be correlated to one another, and that data be available in a sufficient number of solvents (at least four). This analysis has been applied successfully to kinetic data for several heterogeneous ET reactions [30, 45, 77] and is especially useful in obtaining an estimate of the parameter θ . Weaver [11] has strongly criticized this method of analysis, pointing out that there is a weak correlation between $\ln \tau_L$ and $(1/\epsilon_{op} - 1/\epsilon_s)$. This point is illustrated in Figure 2 on the basis of parameters for 15 polar solvents. A very weak correlation is present for the group of solvents considered ($r = 0.733$), the value of the Pekar factor becoming smaller as the value of $\ln \tau_L$ increases. Obviously, any properly performed statistical analysis must take this into consideration, but

the degree of correlation seen for the 15 solvents chosen would not preclude an analysis of kinetic data obtained provided the level of experimental error in the standard heterogeneous ET rate constant is low. The data presented in Figure 2 also demonstrate that one must design experimental studies of solvent effects with careful consideration of the degree of correlation between $\ln \tau_L$ and the Pekar factor. For example, Phelps et al. [80] recently reported a study of solvent effects on the electrooxidation of several sesquibicyclic hydrazines in seven polar solvents, namely, AC, AN, NM, DMF, DMSO, NB and MeOH. The correlation between $\ln \tau_L$ and the Pekar factor is more important for this group of solvents ($r = 0.895$) so that one has no hope of separating the contributions from the pre-exponential factor and the activation barrier on the basis of equation (17) and less objective methods must be used to assess these data. A more careful selection of solvents used would have allowed firmer conclusions to be made about the role of the solvent for these systems.

Other techniques for analyzing the solvent effect involve assuming that one of the solvent dependent terms is known, correcting the observed rate constant for it, and then examining the other solvent effect with respect to the corrected rate constant [11]. For instance, if one assumes values for ΔG_{OS}^* , one may write equation (16) as

$$\ln k_s + \Delta G_{OS}^*/RT = \ln A - \Delta G_{IS}^*/RT - \theta \ln \tau_L \quad (18)$$

It follows that a plot of the left hand side of equation (18) against $\ln \tau_L$ should yield the parameter θ . This procedure was followed in two recent studies [80, 81] using the continuum estimates of ΔG_{OS}^* (equation 2) with R (imaging) set equal to infinity. These estimates of ΔG_{OS}^* are almost certainly high by at least 1 RT and perhaps by as much as 4 RT depending on the nature of the reaction, so that the analyses are of doubtful value. A more interesting method of estimating ΔG_{OS}^* is by using the optical energies for intramolecular electron transfer in bis(ferrocenyl) acetylene cation and related compounds [11, 82, 83]. Thus, the energy associated with transfer of one electron from one ferrocene group to the

other across the acetylene bridge is assumed to be directly related to the value of ΔG_{os}^* for homogeneous ET between ferrocene and ferrocenium cation in a given solvent. The estimates of ΔG_{os}^* from these data are approximately 85 percent of those obtained by the continuum model and therefore closer to estimates based on the MSA results (Table 1). They have mainly been used in the analysis of data for homogeneous ET involving the metallocenes [11]. This method of estimating ΔG_{os}^* is considered in more detail below.

A method applied in the case of perfectly adiabatic reactions ($\theta = 1$) made use of equations (2) and (12), so that the standard rate constant was corrected for solvent dependence of the pre-exponential factor [84, 85].* * This method is not of great interest now considering the body of evidence which indicates that equation (2) overestimates the value of ΔG_{os}^* .

Some mention should be made of the model for solvent effects in heterogeneous rate constants proposed by Abbott et al. [67] on the basis of data for the oxidation of ferrocene in 16 non-aqueous solvents. These authors ignored possible dependence of the pre-exponential factor of the rate constant on solvent relaxation, and attributed solvent dependence to variation in ΔG^* with solvent basicity, acidity, polarity, and polarizability. Indeed, the thermodynamic properties related to ion solvation can be related to solvent basicity in the case of cations and solvent acidity in the case of anions [134], but ion solvation at optical frequencies has not been considered on the basis of the models which they discuss. Considering the poor quality of most correlations reported by Abbott et al. [67] and the probability that their kinetic data are strongly influenced by IR drop, the conclusions reached in their study are difficult to accept.

* In reference [85], the method was incorrectly applied to some reactions which are not perfectly adiabatic ($\theta < 1$).

The general picture which has emerged recently is that the solvent contribution to the pre-exponential factor can vary over a wide range of values of θ . Available data in the literature were examined by the present authors [33] who showed that the magnitude of θ was connected to the magnitude of the rate constant observed in a given solvent. Accordingly, as the reaction becomes slower the value of θ decreases (see Figure 1). This is attributed to a larger contribution to the activation barrier from internal vibrational modes, and/or weak reaction adiabaticity. When θ is sufficiently small one can observe a linear correlation between the logarithm of the standard rate constant and the Pekar factor, as noted by Weaver et al. [86] for the tri(hexafluoroacetylacetonato) ruthenium(III) system.

In conclusion, although many studies of solvent effects have now been carried out, and the presence of a dynamic effect clearly established, one cannot assess the role of the solvent on the basis of these data alone. This is chiefly because one does not have a good method of estimating the activation barrier except for the simplest systems. One way around this problem is to determine the activation enthalpy for the reaction by studying the temperature dependence of the heterogeneous rate constant. These experiments are considered in the following section.

5. The Experimental Activation Enthalpy

Studies of the temperature dependence of the standard rate constant for heterogeneous ET are particularly useful when they are available in different polar solvents, and also for both the homogeneous and heterogeneous reaction. On the basis of equation (15), the experimental activation enthalpy is given by equation (19)

$$\Delta H_{\text{ex}}^* = -R \frac{\partial \ln k_s}{\partial (1/T)} = \Delta H_{\text{is}}^* + \Delta H_{\text{os}}^* + \theta \Delta H_L \quad (19)$$

where ΔH_{is}^* is the inner sphere activation enthalpy, and ΔH_L , the enthalpy arising from the temperature dependence of the longitudinal relaxation time. The latter quantity depends on the temperature dependence of the Debye relaxation time, τ_D , and the high frequency and

static dielectric constants, ϵ_∞ and ϵ_s (equation 13). Values of the temperature coefficients of ϵ_D and ϵ_s are available for most polar solvents [87] and that for ϵ_∞ can be estimated from the temperature coefficient of the refractive index of the solvent [88]. ΔH_L is not insignificant and varies from $\sim 4 \text{ kJ mol}^{-1}$ in fast solvents to $\sim 13 \text{ kJ mol}^{-1}$ in slow solvents.

Solvent dependent ΔH_{ex}^* data have been collected for a number of heterogeneous ET reactions including the electroreduction of cobaltacinium cation [69], cobaltocene [88], the acetylacetonato complexes of Mn^{III} and Fe^{III} [77], benzophenone [45] and a manganese^{III} porphyrin [79]. Data are also available for the electrooxidation of ferrocene [53, 70] and tetrathiofulvalene [78]. In general, one finds that the value of ΔH_{ex}^* increases with increase in solvent viscosity. This result demonstrates that the dynamic solvent effect expressed through the ΔH_L term in equation (19) is present in these data. The most interesting system from the point of view of heterogeneous ET is cobaltocene because this molecule may be both oxidized to a cation and reduced to an anion. On the basis of the FB model, the activation parameters for these reactions should not be the same, whereas the Marcus model predicts that they are the same. In addition, activation enthalpy data are available for the homogeneous ET between cobaltacinium cation and the cobaltocene molecule [89]. For these reasons this system is chosen here for more detailed examination.

The available data for the redox reactions of cobaltocene are summarized in Table 3. Where comparisons can be made, it is seen that ΔH_{ex}^* for the homogeneous oxidation reaction is less than that for the corresponding heterogeneous reaction. Furthermore, the value of ΔH_{ex}^* for the heterogeneous reduction reaction is larger than that for the oxidation reaction [88]. The experimental results are often less than the continuum estimates of ΔH_{os}^* (see Table 1). Keeping in mind that there are contributions to ΔH_{ex}^* from the inner sphere activation enthalpy and the longitudinal relaxation enthalpy, these data strongly confirm that the continuum estimates of ΔH_{os}^* are too large. One method of testing the models considered here is to plot $\Delta H_{ex}^* - \Delta H_{os}^*$ against ΔH_L and obtain θ from the slope and ΔH_{is}^* from the

intercept [88]. These plots using the FB estimates of ΔH_{os}^* are shown in Figure 3 for both the homogeneous and heterogeneous data. Reasonable linear plots are obtained for both cases, the slope being larger for the homogeneous data. It would seem that the FB model overestimates the activation parameters for the homogeneous case perhaps due to effects related to the fact that the two reactants are close to one another in the transition state. This conclusion is supported by the observation that the intercept which gives ΔH_{is}^* is significantly smaller than independent estimates of this quantity (2.1 kJ mol⁻¹ [89]). When the same analysis is applied to the heterogeneous data, very striking results are obtained using the FB model, the data for the electroreduction of cobaltacene lying on the same line as those for the electrooxidation of the same molecule. These results support the proposition that differences in the solvation of cations and anions at static frequencies must be considered in estimating the activation parameters for ET reactions [23].

Comparison of homogeneous and heterogeneous data for ΔH_{ex}^* for other systems demonstrates other features of ET reactions. In the case of 1,4-diaminobenzene, the values of ΔH_{ex}^* determined for the heterogeneous reaction in AN and DMF [90] are much larger than the corresponding quantities for the homogeneous reaction [91]. This is certainly due in part to the fact that there is a dynamic solvent effect in the heterogeneous reaction [73] whereas it is absent for the homogeneous system [30, 92]. A more detailed analysis is not possible because data are available for only two solvents. Similar comments apply to the tetrathiafulvalene system [78].

Particularly interesting results were described recently by Mu and Schultz [79] who demonstrated both on the basis of rate constants and activation enthalpies for the reduction of a Mn^{III} porphyrin in six aprotic solvents that a dynamic solvent effect is present for a system with a quite large inner reorganization energy ($\Delta G_{is}^* = \Delta H_{is}^* \approx 16$ kJ mol⁻¹). These results suggest that factors other than those usually considered [1-4, 9, 11, 28] are important in determining the degree of reaction adiabaticity and hence, the magnitude of the dynamic

solvent effect. The reactant in this study is clearly non-spherical, and the authors obtained an estimate of an effective radius on the basis of diffusion coefficient data. However, their estimates of ΔG_{OS}^* and ΔH_{OS}^* were based on the continuum model and therefore are probably too large. As a result, the estimate of θ based on the solvent effect at 25 °C was different from that obtained from the activation enthalpy data [79]. When the FB model is used to estimate these quantities, the value of θ from the two analyses is the same (~ 0.7).

It is clear that studies of the temperature dependence of the standard rate constant in a series of polar solvents gives an additional powerful tool for examining the nature of the ET step. Under these circumstances one can assess the degree of reaction adiabaticity provided one has a way of estimating the effective radius of the reactant. This subject is discussed in the following section.

6. Effects Of The Reactant

When one examines the data available in the literature, one finds that the standard rate constant in a given solvent varies by four orders of magnitude with the nature of the reactant [33]. Much of this change is usually associated with variation in ΔG_{is}^* within the group of reactants considered, but some is also due to changes in ΔG_{OS}^* . In order to estimate the latter contribution, an estimate of the effective radius of the reactant is needed. For this reason, much experimental effort has been directed in the recent past to studying the metallocenes which are simple from the point of view that they can be represented to a good approximation as spheres [26]. The same comment applies to buckminsterfullerene whose heterogeneous ET kinetics have been studied more recently [57, 61, 93]. For this system, quite good estimates of ΔG_{OS}^* and ΔH_{OS}^* were made using the FB model assuming that the effective reactant radius is equal to the crystallographic radius (360 pm) plus the van der Waals radius of carbon (70 pm) [93].

However, most reactants are not spherical and other methods must be used to deal with the shape of the molecule and the charge distribution within it. Early work by Peover and Powell [94] involved the study of the kinetics of electroreduction of nitrocompounds. As the charge on the anion radical formed became more delocalized, say on a benzene ring, the rate of reaction increased. A similar effect was observed in the electroreduction of a series of quinones, the standard rate constant increasing with increase in the number of benzene rings in the series benzoquinone < naphthoquinone < anthraquinone [95].

Fawcett and Kharkats [96] extended the model proposed by Peover and Powell [94] to take into account the volume correction terms when the reactant is represented as two contiguous conducting spheres. The expression for the effective radius r_e for such a system neglecting the effect of images is

$$r_e = \left[\frac{f_1^2}{a} + \frac{f_2^2}{b} + 2 \frac{f_1 f_2}{c} - f_1^2 F(c, b) - f_2^2 F(c, a) \right]^{-1} \quad (20)$$

where

$$F(r_x, r_i) = \frac{r_x}{2(r_x^2 - r_i^2)} \left[\frac{r_i}{r_x} - \left(1 - \frac{r_i^2}{r_x^2} \right) \ln \frac{r_x + r_i}{(r_x^2 - r_i^2)^{1/2}} \right] \quad (21)$$

Here f_1 and f_2 are the fractions of the total charge on spheres 1 and 2, respectively, a , the radius of sphere 1, b , the radius of sphere 2, and c , the distance between the centers of the spheres. For contiguous spheres, it is obvious that c is equal to $a + b$. The first three terms represent the effect of the charges on the spheres without consideration of the fact that part of the solvation atmosphere of a given sphere is excluded by the proximity of the other sphere. The fourth and fifth terms account for the effects of the finite volume of each sphere. It is clear that the excluded volume terms result in an increase in the effective radius of the reactant, and thus, in a decrease in ΔG_{os}^* . The effect is small if the radii of the two spheres are equal but increases in importance as the relative sizes of the spheres changes [96]. The effective radius can be used in the MSA model to obtain an improved estimate of ΔG_{os}^* , for example, by replacing r_A in equation (7) by r_e .

Fawcett and Fedurco [45] recently extended the above model to the benzophenone system which was represented as three contiguous spheres with each sphere in contact with two others. Two equal size spheres enclosed each of the phenyl rings and a smaller sphere surrounded the carbonyl group. In this case the excluded volume effect is more important. When the diameters of the contiguous spheres are defined by the structure of the molecule, such a model probably underestimates the extent of the solvation because of the chosen spherical shape for each part of the molecule. A better representation would involve contiguous ellipsoids, each extending somewhat further beyond the extreme parts of the molecule. However, a model with ellipsoids would involve more adjustable parameters and therefore would be less easily justified by experiment.

The excluded volume effect can also be used to explain the fact that the activation enthalpy for the homogeneous ET involving the cobaltacinium (+/0) system is slightly smaller than that for heterogeneous ET (see Table 3). On the basis of the work of Kharkats [97], ΔG_{os}^* for homogeneous transfer of one electron between a spherical reactant of radius, a , and another radius, b , is given within the context of Marcus continuum theory by (equation 22)

$$\Delta G_{os}^* = \frac{N_0 e_0^2}{16\pi \epsilon_0 r_e} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (22)$$

where

$$r_e = \left[\frac{1}{a} + \frac{1}{b} - \frac{2}{c} - F(c,a) - F(c,b) \right]^{-1} \quad (23)$$

The quantities c and $F(c, r_i)$ have the same meaning as given above. When the spheres have equal radii and are in contact the value of ΔG_{os}^* is six per cent smaller than predicted when the excluded volume terms are ignored. This correction can also be made within the context of the MSA, the resulting relationship being

$$\Delta G_{os}^* = -\frac{N_0 e_0^2}{16\pi \epsilon_0} \left[\left(1 - \frac{1}{\epsilon_{op}}\right) \frac{1}{r_e} - \left(1 - \frac{1}{\epsilon_s}\right) \frac{1}{(r_e + r_s/\lambda_i)} \right] \quad (24)$$

A different approach to dealing with the effects of molecular shape has been used by Grampp et al. [78, 91, 92, 98]. In their work, the molecule is represented as an ellipsoid with semiaxes a , b and c . This approach has been applied especially to data for homogeneous self-exchange reactions involving organic molecules such as 1,4-diaminobenzene and its derivatives, tetracyanoethylene, tetracyano-*p*-quinonedimethane, and tetrathiofulvalene [98] but also to heterogeneous ET reactions [78]. Such a description of the system requires more parameters than a model based on two contiguous spheres. When applied to a diabatic system with data available both as a function of solvent and temperature [91, 92], a detailed assessment of the mutual orientation of the reactants in the transition state is possible [98]. To date this approach has been limited to the Marcus continuum model for ΔG_{os}^* but it could be easily extended to a non-primitive model such as the MSA.

It should be emphasized that the above models have treated the reacting system as a conductor. There may be circumstances when such an assumption is not appropriate as discussed by German and Kuznetsov [99, 100]. These authors have considered the effects of polarizability on the estimation of ΔG_{os}^* , and also developed models in which the reactant is represented as a dielectric cavity of given shape with embedded point charges. Hupp et al. [101] have shown that a dielectric cavity model is successful in accounting for the solvent dependence of optical intervalence charge-transfer absorption frequencies for symmetrical mixed-valence compounds. Charge transfer within the species $(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{-4,4'-bipyridine-Ru}^{\text{II}}(\text{NH}_3)_5^{5+}$ was treated as dipole inversion within a low dielectric cavity, the length of the dipole (0.51 nm) being based on intervalence Stark effect measurements [102]. On the other hand, a model based on conducting spheres separated by a fixed distance (equation 22) did not give a reasonable description of the same data. These authors obtained their

spectroscopic data in very dilute solutions thereby avoiding the effects of ion pairing on the spectral features. If the model based on two conducting spheres is valid, the absorption frequency observed in various solvents should be linear in the solvents' Pekar factor with a slope determined by the geometrical parameters for the system (equation 23). Although this plot is linear [101] the slope is much less than what one would expect on the basis of reasonable values for the size parameters. A similar result is obtained on the basis of data for the bis(ferrocenyl) acetylene cation [11, 82, 83]. The analysis carried out by Hupp et al. [101] is quite important because it suggests that model compounds based on a redox couple connected through a non-conducting bridge are not good systems for estimating the Gibbs activation energy for homogeneous ET involving the same redox couple.

Other compounds for which interesting structural effects are seen in association with ET are metalloporphyrins [79, 134-137] and oligo-decker sandwich compounds [138]. An important question in metalloporphyrin redox chemistry is whether ET takes place at the metal ion or to the porphyrin ring. Mu and Schultz [135] showed that the porphyrin centered oxidation of Mn^{III} tetraphenylporphyrin chloride is much faster than the metal centered reduction of the same compound. This observation was attributed to the fact that the effective radius of the reactant is much larger in the oxidation reaction in which the charge density is distributed over the porphyrin ring and therefore, ΔG_{os}^* correspondingly smaller.

Anxolabéhère et al. [136] obtained kinetic data for the reduction of some tetraphenylporphyrins and related compounds of more complex structure in DMF, and concluded that solvent reorganization plays an important role in these fast heterogeneous ET reactions. Fawcett et al. [137] examined the redox chemistry of a stable Zn isoporphyrin, and concluded on the basis of the kinetic parameters and their comparison with those for Zn octaethylporphyrin that ET takes place on the ring rather than to the central metal ion. Interpretation of these data is greatly facilitated when activation parameters are measured [79, 137].

Michels and Schmickler [138] have reported a study of heterogeneous ET involving oligo-decker sandwich compounds. These molecules are based on metallocenes with 2,3-dihydro-1,3-diborol as a bridging ligand, a basic example being 1,3,4,5-tetraethyl-2-methyl-1,3-diborolyl-bis(cyclopentadienyl) iron (BlFc). Many of these molecules can be both oxidized and reduced, and undergo some degree of inner sphere reorganization [138]. In the case of the iron compound (BlFc), the rate constant for the oxidation process was 20 times larger than that for reduction at an Au electrode in dichloromethane. The corresponding activation enthalpies were 13.5 and 18.3 kJ mol⁻¹ for the oxidation and reduction steps, respectively. These results suggest that inner sphere reorganization is not important for the iron compound, and support the general conclusion of the FB model that ΔG_{os}^{\ddagger} to form a cation in oxidation of a molecule should be less than that to form an anion. Further studies of these systems would be interesting with respect to this question and others discussed in this review.

In summary, considerable progress has been made in recent years to develop reliable methods of estimating the effective size of the reactant involved in heterogeneous ET. As the theory of ion solvation develops to deal with non-spherical ions on the basis of non-primitive models one can expect a corresponding improvement in understanding the role of reactant shape in determining ET parameters.

7. Double Layer Effects

Most recent studies of heterogeneous ET have involved redox couples in which the most highly charged species is a monovalent cation or anion. Thus, an organic or organometallic molecule is involved in the reaction. This choice is made in order to minimize double layer effects and effects due to ion pairing in the bulk of the electrolyte solution. For this reason much less attention has been paid to redox couples involving transition metal complexes of higher charge in spite of the fact that such systems are often easier to model with respect to structural effects.

The choice of electrolyte is also important in establishing electrostatic conditions at the electrode/solution interface. In organic solutions, the electrolyte is most often a tetraalkylammonium (TAA^+) salt with a hard anion such as perchlorate, tetrafluoroborate or hexafluorophosphate. These systems are chosen to avoid ion pairing problems which occur when smaller ions are used, or problems with ionic adsorption on the electrode. For example, the anion radicals formed from nitro compounds strongly associate with alkali metal cations [103, 104]. In addition, the presence of halide ions in the electrolyte makes the interpretation of kinetic data obtained positive of the potential of zero charge very difficult because these ions are strongly adsorbed on polarizable metals from all known polar solvents [105]. TAA^+ ions also adsorb on the electrode but the nature of the adsorption appears to be more electrostatic rather than chemical in character with solvophobicity also playing a role. These ions also form aggregates with some anion radicals, notable examples being the strong ion associates found between C_{60}^- and $\text{C}_{60}^=$ anions and TAA^+ cations [57].

When heterogeneous ET occurs at potentials negative of the point of zero charge in the presence of TAA^+ ions, it is found that the standard rate constant decreases with increase in the size of the alkyl group [106-113]. On the other hand, the activation enthalpy is relatively independent of cation size [45, 106, 108, 112, 113]. Another observation is that the relative magnitudes of the inhibitory effect increases as the electrode potential is made more negative [111]. These observations can be rationalized if it is assumed that the TAA^+ ions are contact adsorbed on the electrode to form a monolayer whose thickness and extent depend on the size of the ion and electrode potential [111-113]. On the basis of capacity data, it was suggested [113] that the alkyl arms of these ions are bent when the arm contains more than three carbon atoms so that the distance of closest approach of the central nitrogen atom is approximately constant for the larger ions. Using this model, it was possible to explain the decrease in standard rate constant on the basis of electron tunnelling through a layer of TAA^+ ions [114-116]. The fact that the activation enthalpy depends only on the solvent and not on the size of the TAA^+ ion demonstrates that ET takes place outside of the

adsorbed ionic layer in a region where the reactant and product are still interacting chiefly with surrounding solvent molecules [111, 113].

Other recent work on electron tunnelling through barrier films has involved self-assembled monolayers. Miller et al. [117, 118] used ω -hydroxy thiols to form a self-assembled monolayer on a gold electrode. The thiol functionality at one end of the hydrocarbon chain reacts with gold to form a mercaptide thereby anchoring the molecule to the surface. Interactions between the hydroxy groups at the other end of the molecule and water serve to make the monolayer compact. These authors [117, 118] showed that electron tunnelling is the main mechanism for ET to a redox system outside of the monolayer in solution. By varying the chain length of the molecule forming the self-assembled monolayer they were able to demonstrate that the tunnelling current depends exponentially on film thickness. This corresponds to an exponential decrease in the electronic transmission coefficient κ in equation (8) [115, 116].

Chidsey [119] used a self-assembled monolayer on gold with an electroactive terminal group on a fraction of the anchored groups to study ET through films of varying thickness. The electroactive terminal group was ferrocene, which undergoes fast ET upon oxidation to ferrocinium cation. The effect of the monolayer consisting of hydrocarbon chains with 15 CH_2 groups was to slow the reaction down sufficiently that ET kinetic data could be obtained over a voltage range of almost 2V. Analysis of the dependence of the rate constant on potential provided evidence that the Gibbs activation energy is indeed a quadratic function of potential as predicted by Marcus theory [12]. Chidsey estimated the experimental value of ΔG^* for the ferrocene/ferrocinium system in water to be 20.5 kJ mol^{-1} . This result is significantly lower than the estimate of ΔG_{os}^* in water by continuum theory (25.8 kJ mol^{-1}). The estimate of the same quantity using the FB model is 17.4 kJ mol^{-1} . Considering the fact that a small contribution from inner sphere reorganization must be added ($\sim 1 \text{ kJ mol}^{-1}$), the experimental result is very close to the value predicted by the MSA.

In a similar study by Finklea and Hanshew [120], the redox group was pentamine (pyridine) $\text{Ru}^{3+/2+}$. They found some variation in the experimental estimate of ΔG^* depending on the length of the hydrocarbon chain and whether or not spacer chains were present in the self-assembled monolayer. This suggests that the role of the low dielectric monolayer in determining the value of ΔG_{os}^* is changing in the systems studied. Their results also support the conclusion that ΔG_{os}^* is overestimated by the continuum model (equation 2).

Smith and White [121] have discussed double layer effects on both the thermodynamic and kinetic properties of a self-assembled monolayer modified with a redox couple. Since the redox couple is not present in the bulk of the solution, the equilibrium potential for the surface attached redox couple depends on the local (micro) potentials at the oxidized and reduced forms of the redox couple when these are significantly different from the average potential in the bulk of the solution. These authors [121] estimated the average potential on the plane through the centers of the redox species ϕ^p on the basis of measurable thermodynamic quantities, and showed that when this potential is used to approximate the local potential, a reasonable description of the variation in equilibrium potential of the redox couple with dielectric properties of the interface is possible. They also considered the effect of the charge associated with the redox couple on the current observed in linear sweep voltammetry. The shape of the current-voltage curve was shown to depend on the dielectric properties of the interfacial region, their potential dependence, and the potential of zero charge. The calculations performed were based on the classical Frumkin theory [122, 123] for double layer effects in electrode kinetics. Creager and Weber [124] extended this work by considering double layer effects on the current-time transients observed in potential step experiments involving a self-assembled monolayer modified with a redox couple.

The Frumkin equation for the logarithm of the double layer corrected forward rate constant of the redox couple given in equation (1) is usually written by equation (25)

$$\ln k_f + z_A f \phi^d = \ln k_s + \alpha_a f (\phi^d - E - E_s) \quad (25)$$

where k_f is the forward rate constant, ϕ^d , the average potential drop across the diffuse layer, z_A , the charge on the reactant, E , the electrode potential, E_s , the standard electrode potential, α_a , the apparent transfer coefficient, and $f = E/RT$. The transfer coefficient is termed *apparent* because the actual potential experienced by the reactant may differ from ϕ^d for a variety of reasons which are generally termed discreteness-of-charge effects [125-127]. These effects are most noticeable when discrete charges are fixed at a dielectric discontinuity in the system [128] such as the electrode/solution interface for an unmodified electrode, or the hydrocarbon/solution interface in the systems studied by Chidsey [119] and Finklea and Hanshew [120]. As a result the local potential at an anchored redox system ψ^p may differ significantly from the average value on the plane through their centers, ϕ^p . When this is true, the potential, ϕ^d , in equation (25) should be replaced by the local potential ψ^p [127].

Becka and Miller [129] studied double layer effects at uncharged self-assembled monolayers and showed that the kinetics of heterogeneous ET at the monolayer/solution interface depends both on the charge on the reactant and the composition of the monolayer. The reduction of $\text{Fe}(\text{CN})_6^{3-}$ at a ω -hydroxyl dodecane thiol monolayer was considerably faster than at a dodecanethiol monolayer at potentials negative of the potential of zero charge. The authors attributed the difference to the fact that the self-assembled monolayer terminated with the hydroxy group is less hydrophobic so that the reactant can approach closer to the insulating film. In the case of $\text{Fe}(\text{bipyridyl})\text{CN}_4^+$, the opposite effect is observed, the reaction being faster at the methyl terminated monolayer. This reactant is more hydrophobic and bears a smaller charge. These results can also be partially attributed to discreteness-of-charge effects. Because of the large change in dielectric constant from a low value in the oil-like monolayer (~ 2) to a high value in the aqueous solution (~ 78), the reactant experiences a strong repulsive effect at the monolayer/solution boundary. The electrostatic effect [128] is much more important for the polyvalent $\text{Fe}(\text{CN})_6^{3-}$ ion.

Discreteness-of-charge effects have also been discussed for heterogeneous ET reactions occurring at mercury electrodes in the presence of specifically adsorbed non-reacting ions [130-133]. Three of the systems studied [131-133] involved transition metal complexes in which the metal ion is reduced from the +3 to +2 oxidation state in the presence of specifically adsorbed anions. By carrying out these experiments at constant ionic strength, and examining the changes in the logarithm of the corrected rate constant, $y = \ln k_f + z_A f \phi^d$, with adsorbed charge density, σ_a , at constant potential drop across the inner layer, $E - E_s - \phi^d$, one can examine the electrostatic effects of the adsorbed ions with a minimum in change in other double layer properties (see equation 25). The fact that the adsorbed ions are located at the metal/solution interface means that their electrostatic accelerating effect is significantly reduced by the shielding effect of the metal. If the simple Frumkin equation were correct, the kinetic parameter, y , would be independent of $E - E_s - \phi^d$ for changes in the surface coverage by adsorbed anions. In the case of $\text{Co}(\text{NH}_3)_6\text{F}^{2+}$, y decreases with increase in σ_a as qualitatively expected on the basis of the discreteness-of-charge effect [133]. On the other hand, when an anion such as tetrathionate is reduced in the presence of adsorbed iodide anions, the decelerating effect of the adsorbed charge is overestimated when discreteness-of-charge effects are ignored, and the value of y increases with increase in σ_a [130]. Further analysis of these data [130-133] led to a more detailed description of the double layer effect including the location of the reaction site with respect to adsorbed ions and counter ions.

Double layer effects can be quite important in heterogeneous ET reactions especially when the reactants are highly charged. Analysis of these effects requires that interfacial thermodynamic data be available for the electrolyte system being used. The lack of these data have often been the reason why no attempt has been made to examine the double layer effect in more detail. However, modern experimental techniques, especially those based on impedance allow one to obtain these data relatively easily. Double layer effects at self-assembled monolayers are just beginning to be investigated and provide excellent systems on which theories which have been in the literature for some time can be tested in more detail.

8. Conclusions

Studies of solvent effects for heterogeneous ET reactions have done much to increase the understanding of fundamental aspects of this elementary chemical reaction. This is especially true when kinetic data are obtained both as a function of solvent and of temperature so that the variation in activation enthalpy may also be examined. Studies of the redox reactions of the metallocenes [44, 53, 69, 70, 74, 88, 89, 110] have been especially important because of the fact that the reactants are relatively spherical in shape and undergo very small internal reorganization on ET.

There is strong evidence on the basis of recent experimental work that the activation parameters for outer sphere reorganization are overestimated on the basis of the original Marcus formulation [12]. This is not at all surprising since it is well known from equilibrium solvation data for simple ions that the Born model gives unrealistically high estimates of the Gibbs energy and enthalpy of solvation. The most important feature of any improvement on the Born model is that it recognizes the differences in the solvation of cations and anions. Correspondingly, one expects the rate constant for formation of a cation from a molecule to be faster than that for formation of an anion, all other factors remaining the same. The observation that this is the case for cobaltacene [88, 110] and related compounds [138] is important. This prediction should be examined for other molecules for which these reactions can be carried out.

Examination of the recent literature reveals that heterogeneous ET can be understood in at least as much detail as homogeneous ET. Although one must consider double layer effects in the former case, these can be reduced in importance by careful choice of the electrolyte. Homogeneous ET kinetics has the additional complication that the reactants may assume a particular configuration with respect to one another in the transition state [98]. Such steric effects need to be examined in more detail, but they should be simpler in the

heterogeneous ET reaction where the electrical field due to the charge on the electrode plays an important role [106]. Changes in the nature of the steric effect with the type of ET reaction may be the cause of the differences in the relative ordering of rate constants for various metallocenes seen in the homogeneous and heterogeneous regimes [11].

Self-assembled monolayers with anchored redox groups [119, 120] has provided an interesting new way of studying heterogeneous ET. In these systems, the environment of the redox reaction is entirely different than that at the electrode/solution interface. Thus, the comparison of data obtained in the two systems will provide valuable information on the role of environmental effects in heterogeneous ET.

In conclusion, the understanding of ET has advanced considerably during the last decade, and provided a fruitful area for both theoretical and experimental work. However, many problems remain to be solved, so that work in this area will continue to present a challenge to those who are involved.

Acknowledgement

Recent work from this laboratory discussed in this review was supported by the Office of Naval Research, Washington and by the National Science Foundation, Washington (Grant No. CHE 9008171).

Literature

- [1] L.D. Zusman, Chem. Phys. 1980, 49, 295; *ibid*, 1983, 80, 29.
- [2] I.V. Alexandrov, Chem. Phys. 1980, 51, 449.
- [3] M. Ya. Ovchinnikova, Theor. Exp. Chim. 1981, 17, 651.
- [4] D.F. Calef, P.G. Wolynes, J. Phys. Chem. 1983, 87, 3387.
- [5] A. Kapturkiewicz, B. Behr, J. Electroanal. Chem. 1984, 179, 187.
- [6] W. Harrer, G. Grampp, W. Jaenicke, Chem. Phys. Lett. 1984, 112, 263.
- [7] B. Bagchi, Ann. Rev. Phys. Chem. 1989, 40, 115.
- [8] M. Newton, Chem. Rev. 1991, 91, 767.
- [9] H. Heitele, Angew. Chem., 1993, 105, 378; Angew. Chem. Int. Ed. Engl. 1993, 32, 359.
- [10] P. Barbara, W. Jarzeba, Adv. Photochem. 1990, 15, 1.
- [11] M.J. Weaver, Chem. Rev. 1992, 92, 463; see also M.J. Weaver, G.E. McManis, Acc. Chem. Res. 1990, 23, 294.
- [12] R.A. Marcus, J. Chem. Phys. 1965, 43, 679.
- [13] N. Sutin, Prog. Inorg. Chem., 1983, 30, 441.
- [14] P.G. Dzhavakhidze, A.A. Kornyshev, L.I. Krishtalik, J. Electroanal. Chem. 1987, 228, 329.
- [15] D.K. Phelps, A.A. Kornyshev, M.J. Weaver, J. Phys. Chem. 1990, 94, 1454.
- [16] L. Blum, Chem. Phys. Lett. 1974, 26, 200; J. Chem. Phys. 1974, 61, 1556.
- [17] S.A. Adelman, J.M. Deutch, J. Chem. Phys. 1974, 60, 3935.
- [18] R.A. Marcus, in Special Topics in Electrochemistry, P.A. Rock, editor, Elsevier, Amsterdam (1977).
- [19] P.G. Wolynes, J. Chem. Phys. 1987, 86, 5133.
- [20] G.E. McManis, M.J. Weaver, J. Chem. Phys. 1989, 90, 1720.
- [21] L. Blum, W.R. Fawcett, J. Phys. Chem. 1992, 96, 408.
- [22] W.R. Fawcett, L. Blum, J. Chem. Soc. Faraday Trans. 1992, 88, 3339.

- [23] W.R. Fawcett, L. Blum, Chem. Phys. Lett. 1991, 187, 173.
- [24] Y. Marcus, Ion Solvation, Wiley-Interscience, New York (1985).
- [25] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, 4th edition, Wiley-Interscience, New York (1986).
- [26] L.I. Krishtalik, N.M. Alpatova, E.V. Ovsyannikova, Electrochim. Acta, 1991, 36, 435.
- [27] L. Blum, W.R. Fawcett, J. Phys. Chem. 1993, 97, 7185.
- [28] J.T. Hynes, J. Phys. Chem. 1986, 90, 3701.
- [29] J.T. Hupp, M.J. Weaver, J. Electroanal. Chem. 1983, 152, 1; J.T. Hupp, M.J. Weaver, J. Phys. Chem. 1984, 88, 1463.
- [30] W.R. Fawcett, C.A. Foss, Jr. J. Electroanal. Chem. 1989, 270, 103.
- [31] H.L. Friedman, J. Chem. Soc. Faraday Trans.2, 1983, 79, 1465.
- [32] W.R. Fawcett, C.A. Foss, Jr. Electrochim. Acta 1991, 36, 1767; W.R. Fawcett, C.A. Foss, Jr., J. Electroanal. Chem. 1991, 306, 71.
- [33] W.R. Fawcett, M. Opallo, J. Electroanal. Chem. 1993, 349, 273.
- [34] M. McGuire, G. McLendon, J. Phys. Chem. 1986, 90, 1549.
- [35] W. Nadler, R.A. Marcus, J. Chem. Phys. 1987, 86, 3906.
- [36] J. Barthel, K. Bachhuber, R. Buchner, H. Hetzenauer, Chem. Phys. Letters, 1990, 165, 369; J. Barthel, K. Bachhuber, R. Buchner, J.B. Gill, M. Kleebauer, *ibid*, 1990, 167, 62.
- [37] W.R. Fawcett, Chem. Phys. Letters, 1992, 199, 153.
- [38] R.R. Dogonadze, in Reactions of Molecules at Electrodes, N.S. Hush, editors, Wiley-Interscience, New York (1971) Chap. 3.
- [39] W. Schmickler, J. Electroanal. Chem., 1986, 204, 31.
- [40] M. Fleischmann, S. Pons, D.R. Rolison, P.P. Schmidt, Ultramicroelectrodes, Datatech Systems, Morgantown, NC (1987).
- [41] C.P. Andrieux, P. Hapiot, J.M. Saveant, Chem. Rev. 1990, 90, 723.

- [42] J. Heinze, *Angew. Chem.*, 1993, 105, 1327; *Angew. Chem. Int. Ed. Engl.*, 1993, 32, 1268. see also J. Heinze, *Angew. Chem.*, 1991, 103, 175; *Angew. Chem. Int. Ed. Engl.*, 1991, 31, 170.
- [43] W. Lu, A.S. Baranski, *J. Electroanal. Chem.* 1992, 335, 105.
- [44] K. Winkler, A.S. Baranski, *J. Electroanal. Chem.* 1993, 346, 197.
- [45] W.R. Fawcett, M. Fedurco, *J. Phys. Chem.* 1993, 97, 7075.
- [46] R. M. Penner, M.J. Heben, T.L. Longin, N.S. Lewis, *Science*, 1990, 250, 1118.
- [47] A.S. Baranski, *J. Electroanal. Chem.* 1991, 307, 287.
- [48] K.B. Oldham, *Anal. Chem.* 1992, 645, 646.
- [49] D.O. Wipf, E.W. Kristensen, D.R. Deakin, R.M. Wightman, *Anal. Chem.* 1988, 60, 306.
- [50] A.M. Bond, T.L.E. Henderson, D.R. Mann, T.F. Mann, W. Thormann, C.G. Zoski, *Anal. Chem.* 1988, 60, 1878.
- [51] L.K. Safford, M.J. Weaver, *J. Electroanal. Chem.* 1991, 312, 69.
- [52] A.S. Baranski, *J. Electrochem. Soc.* 1986, 133, 93.
- [53] A.S. Baranski, K. Winkler, W.R. Fawcett, *J. Electroanal. Chem.* 1991, 313, 367.
- [54] A.S. Baranski, *J. Electroanal. Chem.* 1991, 300, 309.
- [55] M. Sluyters-Rehbach, J. Sluyters, in *Comprehensive Treatise of Electrochemistry*, E. Yeager, J. O'M. Bockris, B.E. Conway and S. Sarangapani, editors, Plenum Press, New York (1984), Vol. 9, Chap. 4.
- [56] D.D. Macdonald, *Transient Techniques in Electrochemistry*, Plenum Press, New York (1977) Chap. 7.
- [57] W.R. Fawcett, M. Opallo, M. Fedurco, J.W. Lee, *J. Am. Chem. Soc.* 1993, 115, 196.
- [58] A.J. Bard, M.V. Mirkin, P.R. Unwin, D.O. Wipf, *J. Phys. Chem.* 1992, 96, 1861.
- [59] M.V. Mirkin, A.J. Bard, *J. Electrochem. Soc.* 1992, 139, 3535.
- [60] M.V. Mirkin, T.C. Richards and A.J. Bard, *J. Phys. Chem.* 1993, 97, 7672.
- [61] M.V. Mirkin, L.O.S. Bulhões, A.J. Bard, *J. Am. chem. Soc.* 1993, 115, 201.

- [62] M.A.M. Noel, J.J. O'Dea, R.A. Osteryoung, *J. Electrochem. Soc.* 1992, 139, 1231.
- [63] Z.J. Karpinski, R.A. Osteryoung, *J. Electroanal. Chem.* 1993, 349, 285.
- [64] F. Mahlendorf, J. Heinze, *J. Electroanal. Chem.* 1993, 352, 119.
- [65] M.I. Montenegro, D. Pletcher, *J. Electroanal. Chem.* 1986, 200, 371.
- [66] A. Russell, K. Repka, T. Dibble, J. Ghoroghchian, J.J. Smith, M. Fleischmann, C.H. Pitt, S. Pons, *Anal. Chem.* 1986, 58, 2961.
- [67] A.P. Abbott, C.L. Miaw, J. F. Rusling, *J. Electroanal. Chem.* 1992, 327, 31.
- [68] J. Lavagnini, P. Pastore, F. Magno, *J. Electroanal. Chem.* 1992, 333, 1.
- [69] T. Gennett, D.F. Milner, M.J. Weaver, *J. Phys. Chem.* 1985, 89, 2787.
- [70] L.K. Safford, M.J. Weaver, *J. Electroanal. Chem.* 1992, 331, 857.
- [71] W.R. Fawcett, *Langmuir*, 1989, 5, 661.
- [72] Z. Galus, *Pure Appl. Chem.* 1991, 63, 1705.
- [73] M. Opallo, *J. Chem. Soc. Faraday Trans I*, 1986, 89, 2287.
- [74] G.E. McManis, M.N. Golovin, M.J. Weaver, *J. Phys. Chem.* 1986, 90, 6563.
- [75] M. Opallo, A. Kapturkiewicz, *Electrochim. Acta*, 1985, 30, 1301.
- [76] D.A. Corrigan, D.H. Evans, *J. Electroanal. Chem.* 1987, 233, 161
- [77] W.R. Fawcett, M. Opallo, *J. Electroanal. Chem.* 1992, 331, 815.
- [78] G. Grampp, A. Kapturkiewicz, W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* 1990, 94, 439.
- [79] X.H. Mu, F.A. Schultz, *J. Electroanal. Chem.* 1993, 353, 349.
- [80] D.K. Phelps, M.T. Ramm, Y. Wang, S.F. Nelson, M.J. Weaver, *J. Phys. Chem.* 1993, 97, 181.
- [81] R.M. Nielson, M.J. Weaver, *J. Electroanal. Chem.* 1989, 260, 15.
- [82] G.E. McManis, A. Gochev, R.M. Nielson, M.J. Weaver, *J. Phys. Chem.* 1989, 93, 7733.
- [83] M.J. Powers, T.J. Meyer, *J. Am. Chem. Soc.* 1978, 100, 4393.
- [84] W. Harrer, G. Grampp, W. Jaenicke, *J. Electroanal. Chem.* 1986, 209, 23.

- [85] W.R. Fawcett, C.A. Foss, Jr., J. Electroanal. Chem. 1988, 252, 221.
- [86] M.J. Weaver, D.K. Phelps, R.M. Nielson, M.N. Golovin, G.E. McManis, J. Phys. Chem. 1990, 94, 2949.
- [87] W.R. Fawcett, Chem. Phys. Letters, 1990, 174, 167.
- [88] W.R. Fawcett, M. Opallo, J. Phys. Chem. 1992, 96, 2920.
- [89] R.M. Nielson, G.E. McManis, M.N. Golovin, M.J. Weaver, J. Phys. Chem. 1988, 92, 3441.
- [90] A. Kapturkiewicz, W. Jaenicke, J. Chem. Soc. Faraday Trans. 1, 1987, 83, 2727.
- [91] G. Grampp, W. Jaenicke, Ber. Bunsenges. Phys. Chem. 1984, 88, 335.
- [92] G. Grampp, W. Jaenicke, Ber. Bunsenges. Phys. Chem. 1984, 88, 325.
- [93] W.R. Fawcett, M. Opallo, M. Fedurco, J.W. Lee, J. Electroanal. Chem. 1993, 344, 375.
- [94] M.E. Peover, J.S. Powell, J. Electroanal. Chem. 1969, 20, 427.
- [95] J.O. Howell, R.M. Wightman, Anal. Chem. 1984, 56, 524.
- [96] W.R. Fawcett, Yu. I. Kharkats, J. Electroanal. Chem. 1973, 47, 413.
- [97] Yu.I. Kharkats, Elektrokimiya, 1973, 9, 881.
- [98] G. Grampp, W. Jaenicke, Ber. Bunsenges. Phys. Chem. 1991, 95, 904.
- [99] E.D. German, A.M. Kuznetsov, Electrochim. Acta, 1981, 26, 1595.
- [100] E.D. German, A.M. Kuznetsov, Elektrokimiya, 1990, 26, 931.
- [101] J.T. Hupp, Y. Dong, R.L. Blackburn, H. Lee, J. Phys. Chem. 1993, 97, 3278.
- [102] D.H. Oh, S.G. Boxer, J. Am. Chem. Soc. 1990, 112, 8161.
- [103] B.G. Chauhan, W.R. Fawcett, A. Lasia, J. Phys. Chem. 1977, 81, 1476.
- [104] W.R. Fawcett, A. Lasia, J. Phys. Chem. 1978, 82, 1114.
- [105] M.D. Levi, A.V. Shlepakov, B.B. Damaskin, I.A. Bagotskaya, J. Electroanal. Chem. 1982, 138, 1.
- [106] A.S. Baranski, W.R. Fawcett, J. Electroanal. Chem. 1979, 100, 287.
- [107] D.A. Corrigan, D.C. Evans, J. Electroanal. Chem. 1980, 106, 287.
- [108] C. Russel, W. Jaenicke, J. Electroanal. Chem. 1984, 180, 205.

- [109] A. Kapturkiewicz, M. Opallo, J. Electroanal. Chem. 1985, 185, 15.
- [110] T. Gennett, M.J. Weaver, J. Electroanal. Chem. 1985, 186, 179.
- [111] R.A. Petersen, D.H. Evans, J. Electroanal. Chem. 1987, 222, 129.
- [112] D.H. Evans, A.G. Gilicinski, J. Phys. Chem. 1992, 96, 2528.
- [113] W.R. Fawcett, M. Fedurco, M. Opallo, J. Phys. Chem. 1992, 96, 9959.
- [114] J.W. Schultze, K.J. Vetter, Electrochim. Acta, 1973, 18, 889.
- [115] W. Schmickler, J. Electroanal. Chem. 1977, 82, 65.
- [116] J. Lipkowski, C. Buess-Hermann, J.P. Lambert, L. Gierst, J. Electroanal. Chem. 1986, 202, 169.
- [117] C. Miller, P. Cuendet, M. Grätzel, J. Phys. Chem. 1991, 95, 877.
- [118] C. Miller, M. Grätzel, J. Phys. Chem. 1991, 95, 5225.
- [119] C.E.D. Chidsey, Science 1991, 251, 919.
- [120] H.O. Finklea, D.D. Hanshaw, J. Am. Chem. Soc. 1992, 114, 3173.
- [121] C.P. Smith, H.S. White, Anal. Chem. 1992, 64, 2396.
- [122] A.N. Frumkin, Potensialy Nulevogo Zariada, Izdatel'stvo Nauka, Moscow (1979), Chap. 9.
- [123] P. Delahay, Double Layer and Electrode Kinetics, Wiley-Interscience, New York (1965) Chap. 9.
- [124] S.E. Creager, K. Weber, Langmuir, 1993, 9, 844.
- [125] W.R. Fawcett, S. Levine, J. Electroanal. Chem. 1973, 43, 175.
- [126] W.R. Fawcett, J. Chem. Phys. 1974, 61, 3842.
- [127] W.R. Fawcett, Can. J. Chem. 1981, 59, 1844.
- [128] S. Levine, J. Mingins, G.M. Bell, J. Electroanal. Chem. 1967, 13, 280.
- [129] A.M. Becka, C.J. Miller, J. Phys. Chem. 1993, 97, 6233.
- [130] W.R. Fawcett, K. Markusova, Can. J. Chem. 1982, 60, 2038.
- [131] W.R. Fawcett, K. Markusova, Can. J. Chem. 1983, 61, 2821.
- [132] W.R. Fawcett, K. Markusova, Can., J. Chem. 1984, 62, 1497.

- [133] W.R. Fawcett, P.H. Solomon, *J. Electroanal. Chem.* 1988, 251, 183.
- [134] W.R. Fawcett, *J. Phys. Chem.*, 1993, 97, 9540.
- [135] X.H. Mu, F.A. Schultz, *Inorg. Chem.* 1990, 29, 2877.
- [136] E. Anxolabéhère, D. Lexa, J.-M. Savéant, *J. Phys. Chem.* 1992, 96, 1266.
- [137] W.R. Fawcett, M. Fedurco, K.M. Smith, H. Xie, *J. Electroanal. Chem.* 1993, 354, 281.
- [138] L. Michels, W. Schmickler, *J. Electroanal. Chem.* 1993, 225, 139.

Table 1. Gibbs energy and enthalpy of activation for a simple heterogeneous electron transfer reaction in selected polar solvents according to the Marcus [12], McManis-Weaver (MW) [20], and Fawcett-Blum (FB) models [23]. The reactant radius is assumed to be 0.37 nm and the imaging distance, ∞ . The units for ΔG_{os}^* and ΔH_{os}^* are kJ mol⁻¹.

Solvent	Marcus Model		MSA (MW)		MSA (FB)		
	ΔG_{os}^*	ΔH_{os}^*	ΔG_{os}^*	ΔH_{os}^*	$\Delta G_{os}^*(+/0)$	$\Delta H_{os}^*(+/0)$	$\Delta H_{os}^*(0/-)$
acetone (AC)	23.3	20.8	20.1	20.8	15.3	14.0	18.2
acetonitrile (AN)	24.8	21.2	22.5	21.8	16.1	14.4	19.3
butyronitrile (BuN)	22.5	20.3	19.3	19.8	14.3	13.9	17.6
benzonitrile (BzN)	18.3	16.5	16.5	17.1	9.5	9.0	18.0
dimethylacetamide (DMA)	21.5	18.3	19.6	20.2	13.9	11.9	15.3
dimethylformamide (DMF)	21.7	19.2	19.8	20.4	14.0	12.9	17.6
dimethylsulfoxide (DMSO)	20.5	18.1	19.5	18.7	12.7	12.3	16.7
hexamethylphosphoramide (HMPA)	20.5	19.5	17.7	20.5	13.1	13.4	16.4
methanol (MeOH)	25.2	23.2	23.0	24.1	16.9	16.3	20.9
nitrobenzene (NB)	18.2	16.8	17.0	18.7	8.9	8.8	14.8
nitromethane (NM)	23.3	20.3	21.4	21.2	14.1	12.8	18.4
propylene carbonate (PC)	22.5	19.7	21.3	21.0	13.7	12.9	17.3

Table 2. Kinetic Parameters for the Electrooxidation of Ferrocene at a Platinum Electrode in Acetonitrile from Recent Experimental Studies

Source of Data	Experimental Technique	Standard Rate Constant $k_s/\text{cm s}^{-1}$	Electrolyte ^[a]	Temperature K
Montenegro & Pletcher (1986) [65]	Fast scan cyclic voltammetry	1.1	0.5 M TBABF ₄	room
Russell et al. (1986) [66]	Slow linear sweep voltammetry	0.09	0.1 M TBAP	298
Wipf et al. (1988) [49]	Fast scan cyclic voltammetry	0.95 ± 0.44	0.6 M TBAP	room
Bond et al. (1988) [50]	Fast scan cyclic voltammetry	2.2 ± 0.8	0.5 M TEAP	294
Penner et al. (1990) [46]	Slow linear sweep voltammetry	220 ± 120	0.3 M TBAP	room
Baranski et al. (1991) [53]	High frequency a.c. admittance	2.6 ± 0.3	0.1 M TBAP	285
Abbott et al. (1992) [67]	Cyclic voltammetry	0.0194	0.1 M LiClO ₄	298
Karpinski & Osteryoung (1993) [63]	Short time pulse voltammetry	1.2 ± 0.3	0.5 M TBAPF ₆	298
Mirkin et al. (1993) [60]	Scanning electrochemical microscopy	3.8 ± 0.8	0.52 M TBABF ₄	room

^[a] TEAP and TBAP are abbreviations for tetraethylammonium perchlorate and tetrabutylammonium perchlorate, respectively. TBABF₄ refers to tetrabutylammonium tetrafluoroborate, and TBAPF₆ to tetrabutylammonium hexafluorophosphate.

Table 3. Experimental Values of the Activation Enthalpy ΔH_{ex}^* for Various Redox Reactions of Cobaltocene in Several

Aprotic Solvents Together with the Longitudinal Relaxation Enthalpy for the Solvent ΔH_L

Solvent	Longitudinal Relaxation Enthalpy	Experimental		
		Homogeneous (+/0) [89]	Heterogeneous (+/0) [69]	Heterogeneous (0/-) [88]
	$\Delta H_L / \text{kJ mol}^{-1}$		Activation Enthalpy, $\Delta H_{\text{ex}}^* / \text{kJ mol}^{-1}$	
AC	3.7	18.4	20.9	-
AN	5.6	18.0	18.8	24.4
BuN	6.5	-	-	24.6
BzN	11.9	19.7	-	-
DMA	8.0	-	-	24.6
DMF	6.9	-	20.9	-
DMSO	10.7	20.1	23.0	25.1
HMPA	11.5	23.4	-	-
PC	13.4	-	-	28.0

Figure Legends

- Figure 1.** Plots of the standard rate constant for the electrooxidation of ferrocene (o) [53] and 1,4-diaminobenzene (\diamond) [73] obtained in various aprotic solvents against the longitudinal relaxation time of the solvent using logarithmic scales for both axes.
- Figure 2.** Plot of the Pekar factor for a polar solvent, γ , against its longitudinal relaxation time τ_L on a logarithmic scale. The abbreviations for the solvents are given in Table 1 except for ethanol (EtOH), N-methylpyrrolidone (NMP) and propionitrile (PN).
- Figure 3.** Plot of the difference between the experimental activation enthalpy ΔH_{ex}^* and the estimate of the outer sphere contribution according to the FB model ΔH_{os}^* for redox reactions involving cobaltacene against the activation enthalpy for longitudinal relaxation ΔH_L . The homogeneous reaction is oxidation of cobaltacene (o) and the heterogeneous reaction both oxidation (Δ) and reduction (∇). The solid lines were obtained by linear regression using all the homogeneous (o) or heterogeneous data (Δ , ∇). The ordinate scale for the heterogeneous data has been shifted vertically by 10 kJ mol⁻¹ for clarity. The abbreviations for the solvents are given in Table 1.

Fig. 1 Fawcett & Opello

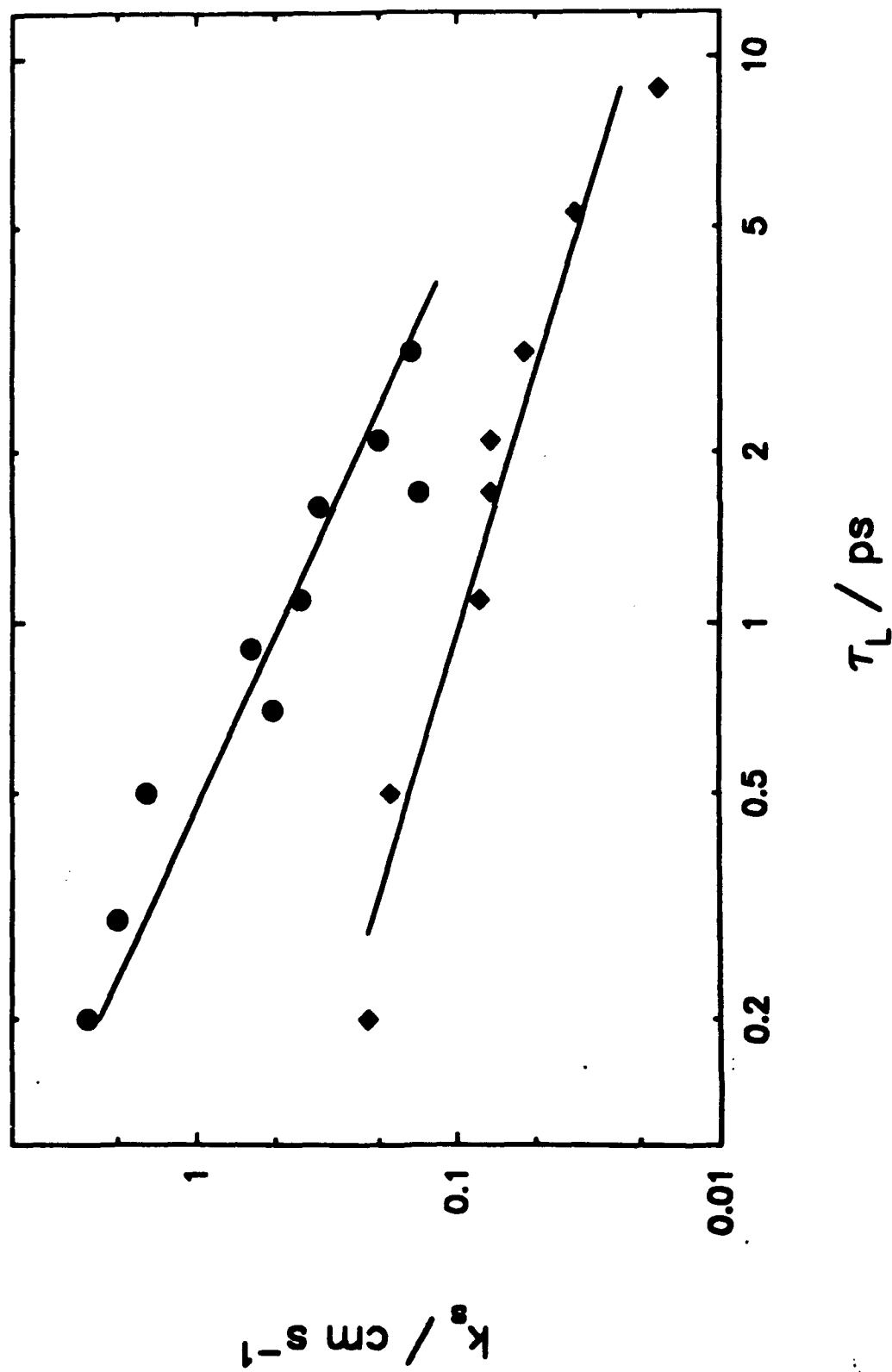


Fig 2 Faure et al + Opallo

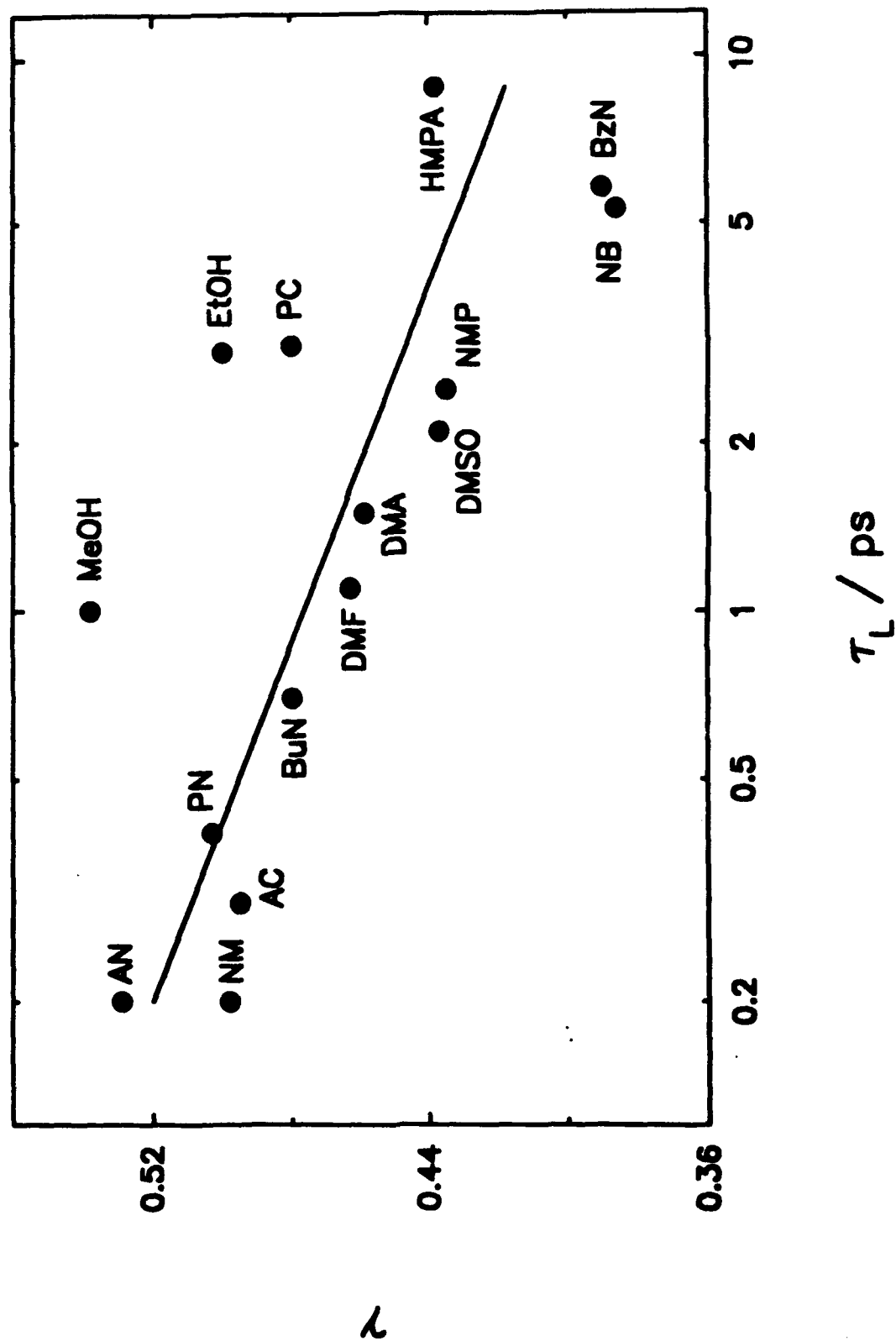


Fig 3. Fawcett + Opallo

